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22 May 1995

1(7)

FROM Japanese unexamined patent application (kokai)  
No. 57-21591 (4 February 1982)

FOR KEMIRA CHEMICALS OY, Information and Patent Service  
P.O. Box 44, FIN-02271 ESPOO, FINLAND

ORDER Order letter of 25 April 1995 by  
Kaisu Välimaa

(19) Japanese Patent Office (JP)  
(12) UNEXAMINED PATENT APPLICATION [KOKAI TOKKYO KOHO] (A)  
(11) No. of publication 57-21591  
(43) Date of publication 4 February 1982

(51) Int. Cl.<sup>3</sup> (IPC) D 21 C 9/16  
Further classification -  
Examiner 7921-4L  
No. of inventions 1  
Request of examination yes  
(Total 6 pages)

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(54) METHOD OF PEROXIDE BLEACHING OF WOOD PULP

(21) No. of application 55-94811  
(22) Date of filing 11 July 1980

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**SPECIFICATION****1. Name of the invention**

Method of peroxide bleaching of wood pulp

**2. Claims**

1. A method of bleaching wood pulp by peracetic acid solution containing hydrogen peroxide, characterised in that after the peracetic acid bleaching is finished, the remaining hydrogen peroxide is activated by adding alkali, and then hydrogen peroxide bleaching is carried out.
2. A method of bleaching wood pulp according to Claim 1, characterised in that peracetic acid bleaching is carried out after the wood pulp has been treated by acid, chelating agent or phosphate.

**3. Detailed description of the invention**

This invention is related to a method of peroxide bleaching of wood pulp. In more detail, it is related to a method of improving the bleaching effect in the peracetic acid bleaching of wood pulp by means of adding alkali after the peracetic acid bleaching, and then hydrogen peroxide bleaching is carried out by means of the remaining hydrogen peroxide.

Peracetic acid is manufactured by the automatic oxidation of acetaldehyde or the acetylation of hydrogen peroxide, and mainly the product prepared by the latter method is used in bleaching. In this manufacturing method, hydrogen peroxide and glacial acetic acid or acetic acid anhydride are reacted according to the following reaction formulae:



The product of formula (1) is called the equilibrium peracetic acid and is sold as peracetic acid for industrial use; an example of its composition is 42 % peracetic acid, 6 % hydrogen peroxide, 37 % acetic acid, 14 % water and 1 % sulphuric acid.

The product of formula (2) is also called the in situ method peracetic acid, and it can be prepared easily in the factories where peracetic acid is used, e.g. pulp mills etc., from low-concentration hydrogen peroxide and acetic acid anhydride; an example of its composition is 23 % peracetic acid and 8 % hydrogen peroxide.

The products of both methods can be used for pulp bleaching, but hydrogen peroxide coexists in the prepared peracetic acid solutions.

Depending on the pulp to be bleached and the quality required, the bleaching of wood pulp by these peracetic acids is carried under different conditions, but generally it is done at the pH of 2-8, the pulp concentration of 8-15 %, the temperature of 40-80 °C and the time of 1-3 hours.

Peracetic acid bleaching has been studied in the bleaching of different pulps. In the bleaching of mechanical pulp, the decreasing of yield by bleaching is small, and a good bleaching effect is obtained. Peracetic acid is also used as a regulating reagent in the extraction of holocellulose from wood, and since it has a superior delignification effect without damaging carbohydrates, it has been also studied in the bleaching of chemical pulp. Especially for preventing the pollution caused by bleaching waste waters as required recently for the protection of environment, the switching over from the conventional chlorine bleaching to the oxygen based bleaching is studied, and here attention is paid to the superior delignification effect and bleaching power of peracetic acid.

For example in the examined Japanese patent application (kokoku) No. 54-11402 (1979), due to the fear that waste waters from the chlorine bleaching treatment of Kraft pulp are poisonous for fish, a three-stage bleaching of D-PA-D (where D means chlorine dioxide bleaching and PA peracetic acid bleaching) comprising a peracetic acid bleaching is proposed as a bleaching process excluding the chlorine treatment, having the effect that bleaching to a brightness of 80 % or higher is possible without damaging the yield or the pulp viscosity.

Moreover, as a bleaching processes based only on oxygen bleaching, not containing chlorine ions in the waste water and making it possible to recover and use the waste water, and finally concentrate and burn it in a recovery furnace, the three-stage bleaching O-PA-P (where O means oxygen bleaching and P means hydrogen peroxide bleaching) comprising the peracetic acid bleaching, the three-stage bleaching P-PA-P etc. have also been proposed.

As described above, the peracetic acid bleaching has attracted attention as specific oxygen-based bleaching, but it is still in the research stage, not yet being industrially applied. This is due to the fact that peracetic acid is expensive for a bleaching agent, which makes a bleaching process comprising peracetic acid bleaching economically inferior.

In order to reduce the costs of peracetic acid bleaching and to improve its economy, the present inventors examined the solution composition of peracetic acid formed by the acetylation of hydrogen peroxide and studied methods where all peroxides are effectively used for bleaching to increase the bleaching effect, and thus reached this invention.

This invention is a method of bleaching wood pulp by peracetic acid solution containing hydrogen peroxide, characterised in that after the peracetic acid bleaching is finished, the remaining hydrogen peroxide is activated by adding alkali, and then hydrogen peroxide bleaching is carried out.

To explain the method of this invention in more detail, the peracetic acid used in the peracetic acid bleaching is the acetylation product of hydrogen peroxide with coexisting hydrogen peroxide, the added amount is about 0.2-10 % as peracetic acid based on absolutely dry pulp, depending on required brightness and quality, usually added at pH 2-8, preferably at pH 4-6, at the pulp concentration of 5-20 %, preferably 10-15 %, at the temperature of 20-100 °C, preferably 40-80 °C, usually for 30 min to 4 h, preferably for 1-2 h. At this time, for limiting the decomposition of peracetic acid and hydrogen peroxide

by heavy metal catalysts, it is preferable to use also chelating agents, for example polymer phosphates such as sodium tripolyphosphate or aminopolycarboxylates such as EDTA (ethylenediamine tetraacetate).

The pulp with a peracetic acid bleaching completed under the above conditions is not washed, but alkali is then added and blended with the pulp to activate the remaining hydrogen peroxide, and then hydrogen peroxide bleaching is carried out. The alkali agent is usually added 0.5-8 % based on absolutely dry pulp, an amount necessary to make the pH of the pulp slurry 9-11, the treating temperature is 20-100 °C, preferably 40-80 °C, the pulp concentration is 5-20 %, preferably 10-15 %, and bleaching is carried out usually for 30 min to 3 h, preferably 30 min to 2 h.

Further, a still higher brightness can be achieved at this stage by still adding hydrogen peroxide if necessary at the time of alkali addition.

The above bleaching is completed by means of washing, but if a still higher brightness is required, bleaching stages can be multiplied.

As the alkali agent to be used in this invention, hydroxides of alkali metals such as sodium, potassium etc., hydroxides of alkaline earth metals such as calcium, magnesium, etc., or sodium carbonate, ammonium carbonate, sodium phosphate, ammonia etc. can be mentioned.

Further, in order to prevent the decomposition of peracetic acid and hydrogen peroxide by heavy metals, the pulp can be pretreated before the peracetic acid bleaching by acids, organic chelating agents, phosphates etc. and thus its brightness can be still improved. In concrete terms, the pulp before the peracetic acid bleaching is usually diluted to the concentration of 1-5 %, and in the case of acid treatment, it is adjusted to pH 1-5 by mineral acid such as sulphuric acid or hydrochloric acid, or organic acid such as acetic acid or formic acid, then after a given time it is dewatered and heavy metals are removed, whereafter peracetic acid bleaching is carried out. In the case of organic chelating agents, 0.05-0.5 % of EDTA, NTA (nitrilotriacetate), DTPA (diethylenetriaminepentaacetate) etc. is added, pH is adjusted to 5-9 and the same treatment is carried out. In the case of phosphate treatment, 0.5-3 % of sodium metaphosphate, sodium tripolyphosphate, sodium pyrophosphate or the like is added, pH is adjusted to 7-9 and the same treatment is carried out.

The method of this invention can be applied to any pulp, chemical pulp, semi-chemical pulp or mechanical pulp, by adjusting the treating conditions.

The advantage of this invention is that bleaching by the peracetic acid method to a higher brightness than before is possible with lower costs and without damaging the quality of the bleached pulp. Namely, firstly the hydrogen peroxide coexisting with the peracetic acid can be used effectively in bleaching and the bleaching effect can be increased with lower bleaching costs. Then secondly, since the hydrogen peroxide coexisting with the peracetic acid can be used effectively, peracetic acid can be manufactured by the equilibrium method or the in situ method, it is not necessary to stress extremely the hydrogen peroxide to peracetic acid conversion ratio, and the manufacturing costs of peracetic acid can be decreased.

In the following this invention is explained by means of examples. In the examples, brightness was measured by the JIS P 8123 testing method. The reagent addition ratios are given as % by weight based on absolutely dry pulp.

**Example 1**

Hardwood pulp cooked by the Kraft method (LKP) was used as sample. The brightness of this unbleached pulp was 31.5 % and its K value 12.4. A first stage oxygen bleaching was carried out. Its conditions were 3 % NaOH, 0.2 %  $MgSO_4 \cdot 7H_2O$ , pulp concentration 30 %, maximum temperature 100 °C, oxygen pressure 6 kg/cm<sup>2</sup>, temperature increasing time 90 min, keeping time 5 min, treatment in autoclave. The thus treated pulp was diluted to 3 %, dewatered to 25 % and then used as peracetic acid bleaching sample. The brightness of this sample was 46.1 % and its K value 6.8. Then peracetic acid bleaching was carried out with peracetic acid made by reacting acetic acid anhydride and hydrogen peroxide, having the following composition: 45 % peracetic acid, 11.5 %  $H_2O_2$ , 20 % acetic acid and 23.5 % water. Then peracetic acid bleaching was carried out under the following conditions. The results are shown in Table 1.

Table 1. Peracetic acid bleaching.

Peracetic acid (%) $CH_3COOOH$ Coexisting $H_2O_2$ (%)	NaOH (%)	DTPA (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%) $CH_3COOOH$ $H_2O_2$	Brightness (%)
5.0	1.28	5.0	0.5	15	70	2	7.4/5.4	99.9 23.6 73.2

According to the above, 0.98 % of  $H_2O_2$  remained after the peracetic acid bleaching. Then 1.5 % of NaOH was added, and hydrogen peroxide bleaching was carried out. The results are shown in Table 2.

Table 2. Continued hydrogen peroxide bleaching.

Remaining $H_2O_2$ (%)	Added NaOH (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%)	Brightness (%)
0.98	1.5	13	70	2	11.1/9.7	97.3	80.8

According to the above, it was possible to still increase the brightness by means of utilising the remaining  $H_2O_2$ .

## Example 2

Pretreatment was carried out before carrying out the peracetic acid bleaching of Example 1. As pretreatment conditions, the pulp was diluted after the acid bleaching to a pulp concentration of 8 %, and in the case of acid pretreatment, it was adjusted to pH 2 by 4N H<sub>2</sub>SO<sub>4</sub>. In the case of chelating agent treatment, it was adjusted to pH 7 by adding 0.1 % of DTPA. In the case of phosphate treatment, it was adjusted to pH 8 by adding 0.5 % of sodium tri-polyphosphate.

After the above treatments the pulps were left as such for 10 min and then dewatered to 25 %. These pulps were subjected to peracetic acid bleaching under the following conditions. The results are shown in Table 3.

Then NaOH was added to activate the remaining H<sub>2</sub>O<sub>2</sub> and hydrogen peroxide bleaching was carried out. The results are shown in Table 4.

Table 3. Peracetic acid bleaching after pretreatments.

	Peracetic acid (%) CH <sub>3</sub> COOOH Coexisting H <sub>2</sub> O <sub>2</sub> (%)	NaOH (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%) CH <sub>3</sub> COOOH H <sub>2</sub> O <sub>2</sub>	Brightness (%)
No pretreatment	5.0 1.28	5.0	15	70	2	7.4/5.4	99.9 23.6	73.2
Acid pretreatment	5.0 1.28	5.0	15	70	2	7.1/5.2	81.0 6.7	75.8
Chelating agent pretreatment	5.0 1.28	5.0	15	70	2	7.3/5.2	76.4 2.3	77.4
Phosphate pretreatment	5.0 1.28	5.0	15	70	2	7.4/5.3	80.4 5.1	76.1

Table 4. Continued hydrogen peroxide bleaching.

	Remaining H <sub>2</sub> O <sub>2</sub> (%)	Added NaOH (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%)	Brightness (%)
No pretreatment	0.98	1.5	13	70	2	11.1/9.7	97.3	80.8
Acid pretreatment	1.19	1.5	13	70	2	10.8/9.3	92.7	82.9
Chelating agent pretreatment	1.25	1.5	13	70	2	11.0/9.5	87.6	84.2
Phosphate pretreatment	1.22	1.5	13	70	2	11.0/9.7	91.2	83.6

According to the above, the reagent consumption ratio decreased and pulp with a high brightness was obtained by means of the pretreatments.

Example 3

Ezo Todomatsu RGP was subjected to peracetic acid bleaching. The brightness of the unbleached pulp was 51.8 %. After the same acid pretreatment was carried out as in Example 2, peracetic acid bleaching was carried out. The results are shown in Table 5.

Then NaOH was added and the bleaching was continued. The results are shown in Table 6.

Table 5. Peracetic acid bleaching.

	Peracetic acid (%) CH <sub>3</sub> COOOH Coexisting H <sub>2</sub> O <sub>2</sub> (%)	NaOH (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%) CH <sub>3</sub> COOOH H <sub>2</sub> O <sub>2</sub>	Brightness (%)
Acid pretreatment	5.0 1.28	5.0	15	70	2	7.1/5.1	85.7 9.3	64.4

Table 6.

	Remaining H <sub>2</sub> O <sub>2</sub> (%)	Added NaOH (%)	Sodium silicate (%)	Pulp concentration (%)	Temperature (°C)	Time (h)	pH Initial/Final	Reagent consumption ratio (%)	Brightness (%)
Acid pretreatment	1.16	1.8	1.5	13	70	2	11.1/8.9	96.7	69.4

According to the above, even in the case of applying to mechanical pulp, a still higher brightness than before can be obtained.

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Page 6: Corrections of misprints (incorporated in the above translation).